LEVEL II

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IN SEARCH OF STRONG INFRARED EXTINCTION IN AEROSOLS

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INTRODUCTION

There is no optical region more amenable to theoretical treatment of nonspherical and compound particles than the Rayleigh region. Here it is possible to calculate with relative ease, the extinction due to any particle which can be represented by an ellipsoid[1] or a confocally coated ellipsoid[2]. This is not very restrictive because nearly all convex particles can be accurately described by an ellipsoid envelope, with the exception of polyhedra. Coated spheres, needles and discs are accurately represented. Recently lattice dynamical and dielectric continuum calculations were made predicting extinction by Rayleigh cubes and polyhedra[3-5]. It is even possible to model accurately the extinction caused by a collection or irregular shapes, the most common form for solid aerosols. From the standpoint of producing strong extinction per unit mass, the Rayleigh region is the most fruitful for even a moderately absorbing particle. Here extinction as a function of size attains a high plateau which remains independent of size so long as we stay within the region. Here we do not have to depend, as is often the case elsewhere, on narrow extinction resonances which all but disappear when particle size, shape, composition or orientation change only slightly. The Rayleigh region holds the most promise for yielding particles engineered to produce strong broad electromagnetic extinction, and therefore it should be explored as extensively as possible.

DISCUSSION

The Rayleigh region is constrained by definition to be located

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where particle size is small with respect to wavelength both inside and outside the particle. Here there is a close connection linking the static polarization of a particle and its extinction per unit mass. Before describing this connection first we will take a closer look at the extinction per unit mass which will be referred to simply as the extinction. Extinction, γ, determines the fraction of incident radiation, T, which passes a distance, L, through an aerosol cloud having concentration, C, in accordance with Beers Law.

$$T = e^{-\gamma CL}$$

A convenient self-consistent set of units puts extinction in square meters per gram of aerosol, concentration in grams of aerosol per cubic meter of air, and pathlength in meters. The extinction coefficient depends on the geometric cross section, G, optical extinction efficiency factor, Q, and particle weight, W, in the following way.

$$\gamma = \left\langle \left\langle \frac{GQ}{W} \right\rangle_\theta \right\rangle_m$$

The inner brackets represent an average over solid angle to take into account random orientations experienced by particles in the cloud while the outer brackets represent an average over particle mass (size) distribution in the cloud. This double integral simplifies to the following single integral expression because $\langle GQ/W \rangle_\theta$ is independent of particle size for an absorbing particle in the Rayleigh region and of course particle weight is independent of orientation.

$$\left\langle \left\langle \frac{GQ}{W} \right\rangle_\theta \right\rangle_m = \frac{\langle GQ \rangle_\theta}{W}$$

The fundamental extinction theorem relates the extinction cross section, GQ, to the real part of the scatter amplitude in the forward direction, $\mathrm{Re}\{S(0)\}$, for radiation of wavelength, λ.

$$GQ = \frac{\lambda^2}{\pi}\mathrm{Re}\{S(0)\}$$

The Rayleigh theory relates the static complex polarizability, α, of an absorbing particle to its forward scatter amplitude.

$$S(0) = i\,\frac{2\pi^3}{\lambda}\alpha$$

Substituting this value into the fundamental extinction theorem we find for a single particle at one orientation,

$$GQ = \frac{8\pi^2}{\lambda}\mathrm{Re}\{(i\alpha)\}$$

The extinction cross section resulting from a collection of randomly

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oriented ellipsoidal particles can be expressed as a function of a complex polarizability which is just one third the sum of the polarizabilities, α_j, along the major ellipsoidal axes.

$$\alpha = (\alpha_1 + \alpha_2 + \alpha_3)/3$$

The major axis polarizabilities of an ellipsoidal particle are directly proportional to particle volume, V, and depend on complex refractive index, n, and depolarization factors, L_j, along the major ellipsoidal axes a, b, and c.

$$\alpha_j = \frac{V(n^2-1)}{L_j(n^2-1)+1}$$

where $n = N + iK$

$$L_1 = \int_0^\infty \frac{abc\, ds}{2\,(S+a^2)^{3/2}\,(s+b^2)^{1/2}\,(s+c^2)^{1/2}}$$

with appropriate cyclical changes for L_2 and L_3. The three depolarization factors have the properties that each is nonnegative and their sum is one.

The depolarization factors of spheroids depend only on the aspect or axial ratio of the axis of symmetry with respect to either one of the other two equal major axes. For a prolate spheroid with axial ratio, A, defined always to be greater than one;

$$L_1 = \frac{1-e^2}{e^2}\left(-1 + \frac{1}{2e}\ln\frac{1+e}{1-2}\right)$$

$$L_2 = \frac{1-L_1}{2} \quad L_3 = L_2 \quad e^2 = 1-1/A^2$$

For an oblate spheroid with aspect ratio, A, also defined to be greater than one;

$$L_1 = \frac{1+f^2}{f^2}\left(1 - \frac{1}{f}\arctan f\right)$$

$$L_2 = \frac{1-L_1}{2} \quad L_3 = L_2 \quad f^2 = A^2 - 1$$

We may now write the extinction for a cloud of randomly oriented Rayleigh ellipsoidal or spheroidal particles.

$$\gamma = \frac{8\pi^2}{3\lambda W}\sum_{j=1}^{3}\frac{V\,2NK}{\{L_j\,(N^2-K^2) + (1-L_j)\}^2 + (2NKL_j)^2}$$

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When the wavelength and density, ρ, are moved over to the left hand side of the equation, shape dependence is more clearly evident on the right hand side. In this way, wavelength and density, which are altogether unrelated to shape, no longer appear as independent variables and extinction values will not be tied to a single wavelength and density.

$$\gamma\rho\lambda = \frac{16\pi^2}{3}\sum_{j=1}^{3}\frac{NK}{\{L_j(N^2-K^2)+(1-L_j)\}^2+(2NKL_j)^2}$$

It is this quantity $\gamma\rho\lambda$ that we choose to plot on the contour maps. This frees us to select any wavelength, density combination and interpret extinction isopleths accordingly. One self-consistent set of units convenient to use in the infrared holds the extinction in square meters per gram, puts density in grams per cubic centimeter, and wavelength in micrometers. In this system of units, extinction density wavelength contour maps may be said to represent, for example, extinction at one micrometer and unit density or at half a micrometer and a density of two.

When the shape and dielectric properties of the particle combine to reduce the value of the denominator in the previous equation, there is an increase in extinction or equivalently a resonance[6]. The shape dependence of this resonance enters through the depolarization factor. A sphere has depolarization factors equal to 1/3 for fields applied along any orthogonal set of three radial axes. A prolate spheroid approximating a thin needle has $L_j \to 0$ for fields applied parallel to its length and $L_j \to 1/2$ for fields in the plane of symmetry. An oblate spheroid approximating a thin disk has $L_j \to 1$ for fields applied perpendicular to the plane of symmetry and $L_j \to 0$ for fields in the symmetry plane.

A resonance occurs when the following conditions are satisfied:

$$L_j\,(N^2 - K^2) + (1-L_j) = 0 \quad 2NKL_j = 0$$

Remembering that all depolarization factors are nonnegative, we find that for a given shape and depolarization factor the resonant values for the optical constants which satisfy both conditions are

$$N = 0 \quad K = (1/L_j - 1)^{1/2}$$

A close look at extinction in the limit $n \to 0$ and K equal to the above value reveals that this in indeed an extinction pole. All three depolarization factors for a sphere are equal to 1/3 and its resonance therefore occurs at $N=0$ and $K=\sqrt{2}$.

The special case where $L_j \to 0$ warrents some discussion. This can occur, as mentioned before, for selected orientations of needles and disks with respect to the electric field vector. Taking this limit in the previous equation relating extinction to complex refractive index and depolarization factor, the terms in the summation corresponding to depolarization approaching zero become simply

$$\gamma\rho\lambda = \frac{16\pi^2}{3} \sum_{L_j=0} NK + \text{terms with } L_j \neq 0$$

These terms tend to dominate over terms which correspond to depolarization which is nonzero over most of the complex refractive index plane.

Figure 1 shows extinction density wavelength contours for a sphere over a complex refractive index range typical of metals at visible wavelengths and semiconductors at visible and infrared wavelengths. Future references to extinction density wavelength contours will be made simply to extinction for brevity. There is one resonance or region of strong extinction centered at N=0 and $K = \sqrt{2}$. This has been identified as the first electrostatic surface polariton mode. The region where the imaginary component of the refractive index is greater than the real component is the restrahl region. There must always be absorption here in order to satisfy the Kramers-Kronig relationships. Any point lying on the K axis violates this requirement. Therefore the K axis may only be approached, and extinction will always remain bounded. The closest approach to this resonance will be made by a material with maximal oscillator strength in a single oscillator within sum rule limits and with minimal oscillator damping[7].

In figure 2 the single resonance of a sphere has split into two resonances for an oblate spheroid at an aspect ratio of ten. One pole moves down the K axis toward the origin without noticeable changes in the extent of its contour values while the second resonance climbs steadily up the K axis, spreading its influence in the form of high extinction over more and more of the complex index plane while aspect ratio grows. A similar situation applies to prolate spheroids except that the resonance moving down the K axis converges on the value one.

A metal is the aerosol material best suited to take advantage of high extinction produced by the resonance moving up the K axis. A simple model[7] for the optical constants of a metal, the Drude theory model, puts the real parts of the refractive index equal to the imaginary index at wavelengths greater than ten microns. Extinction produced by metal prolate spheroids obeying the Drude theory appears in

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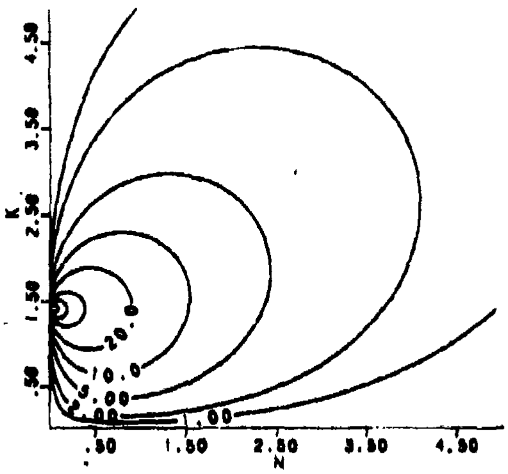

Figure 1 Extinction isopleths for a Rayleigh sphere as a function of the complex refractive index.

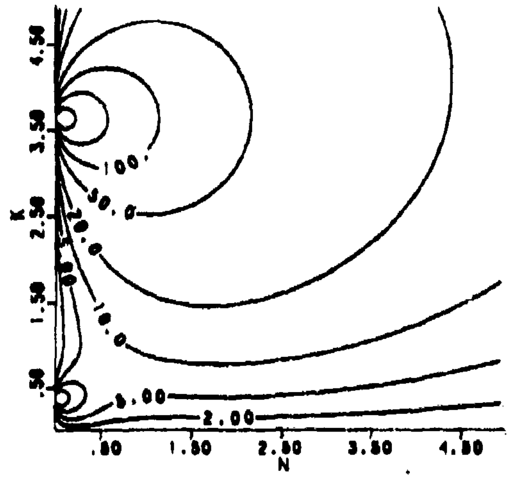

Figure 2 Extinction isopleths for a Rayleigh oblate spheroid with an aspect ratio of ten as a function of complex refractive index.

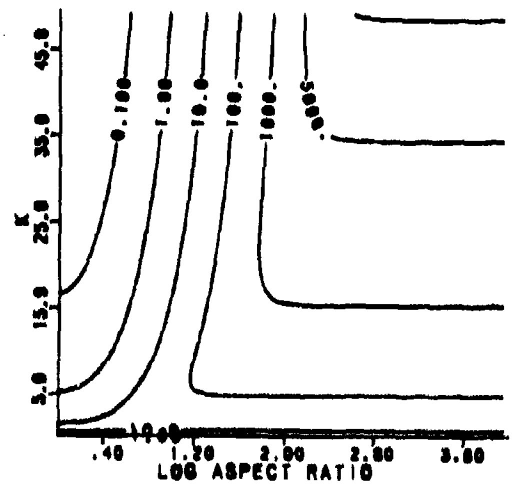

Figure 3 Extinction isopleths for a metal (N=K) Rayleigh prolate spheroid as a function of the base ten log of the aspect ratio and the imaginary part of the complex refractive index.

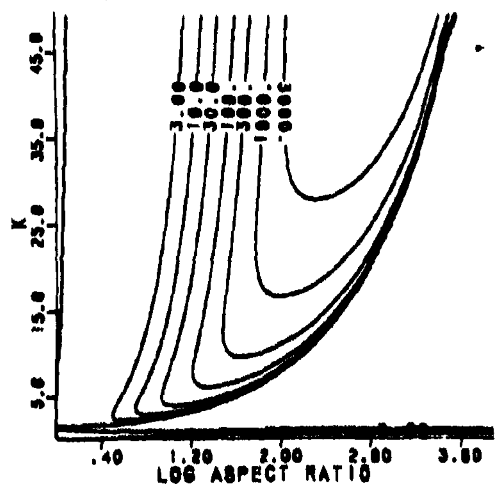

Figure 4 Extinction difference isopleths between metal (N=K) spheroids, prolate minus oblate compared at equal aspect ratio and complex refractive index. Negative isopleths are deleted.

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figure 3 as a function of the base ten logarithm of the aspect ratio and optical constants. This range of optical constants is typical of metals in the infrared. Metal oblate spheroids generate a similar appearing set of contours. In figure 4 extinction produced by a metal oblate spheroid is subtracted from that produced by a prolate spheroid having the same aspect ratio and optical constants. Negative contour values are not plotted. In figure 5 prolate spheroid extinction is subtracted from oblate, so the region where an oblate spheroid is superior to a prolate spheroid appears in the area which is contoured out to an aspect ratio of ten thousand. Increasing metallic refractive index and increasing aspect ratio work to produce high extinction as can be seen in figure 3. When comparing which shape causes higher extinction at a given complex index we see from figure 4 and 5 that the prolate shape is superior for aspect ratios less than some value while the oblate is superior for aspect ratios greater then that value. In comparisons at a fixed aspect ratio, we see that the oblate spheroid is superior below certain complex indices and for higher complex indices a prolate spheroid is better.

The original ellipsoidal theory of Rayleigh has been extended in recent years to include confocally coated ellipsoidal particles. The major axis polarizabilities, α, of a confocally coated ellipsoid are directly proportional to overall ellipsoid volume, V, and depend on inner (core) complex refractive index, n_i, outer (shell) complex refractive index, n_o, core volume fraction, V_i/V, inner depolarization factor, L_i, and outer depolarization factor, L_o.

$$\alpha_j = \frac{V}{4\pi} \frac{(n_o^2-1)\left\{L_i(n_i^2-n_o^2) + n_o^2\right\} + \frac{V_i}{V}(n_i^2-n_o^2)\left\{L_j(1-n_o^2) + n_o^2\right\}}{\left\{(n_i^2-n_o^2)L_i + n_o^2\right\}\left\{1+L_o(n_o^2-1)\right\} + \frac{V_i}{V}L_o(1-L_o)(n_i^2-n_o^2)(n_o^2-1)}$$

Where the depolarization factors and complex indices are defined as before for solid ellipsoids and spheroids. The confocal constraint requires that the difference between the square of the outer axes and the square of the inner colinear axes remain constant, resulting in a thinner coating on larger axes. The value for this constant is determined by the core ellipsoid volume fraction. It is important to recognize that a confocal constraint removes a degree of freedom from simultaneous specification of inner depolarization factor, outer depolarization factor and core volume fraction. Once any two of these variables are specified, the third is automatically determined by the constraint.

If the coated ellipsoid is a coated prolate spheroid, both the inner and outer spheroids will be prolate with two foci points in

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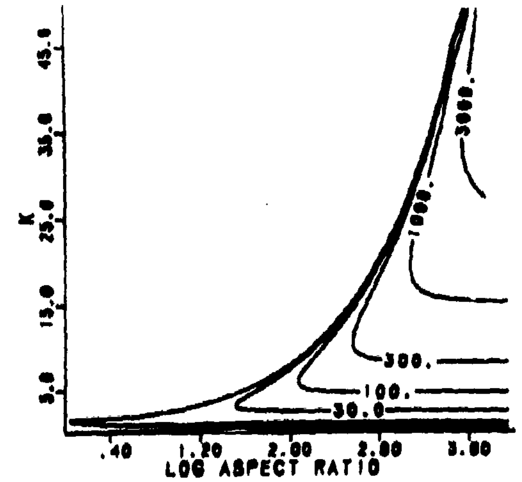

Figure 5. Extinction difference isopleths between metal (N=K) spheroids, oblate minus prolate, compared at equal aspect ratio and equal complex refractive index. Negative isopleths are deleted.

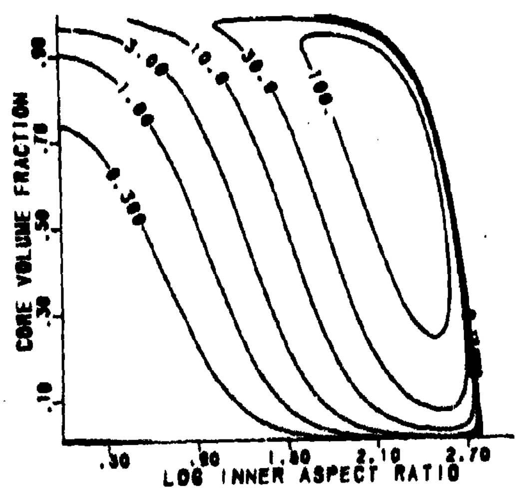

Figure 6. Extinction difference isopleths coated minus homogeneous, between a metal mantle (N=20, K=20) dielectric core (N=1.5, K=.01) oblate spheroid and a homogeneous oblate spheroid of the same metal. Aspect ratios of the core and homogeneous spheroid are equal. Negative contours are deleted.

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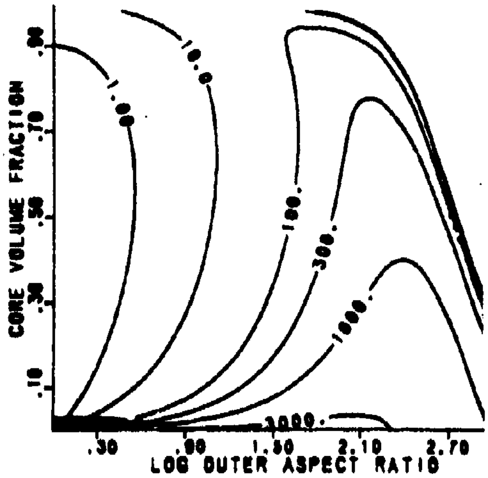

Figure 7. Extinction difference isopleths, coated minus homogeneous, between a metal mantle (N=20, K=20), dielectric core (N=1.5, K=.01) oblate spheroid and a homogeneous oblate spheroid of the same metal. Aspect ratios of the mantle outer surface and homogeneous spheroid are equal. Negative contours are deleted.

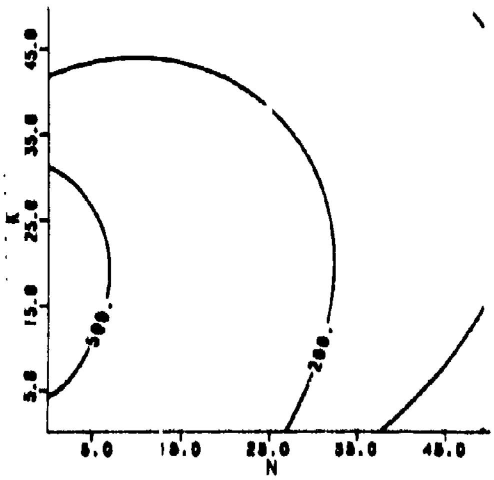

Figure 8. Extinction isopleths for a metal mantle (N=20, K=20) oblate spheroid at an outer aspect ratio of 100 and a core volume fraction of 0.5 as a function of core complex refractive index.

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common, and if it is a coated oblate spheroid then both will be oblate with a foci ring of points in common. Both inner and outer depolarization factors depend upon aspect ratios as they did for solid spheroids. However, due to a constraint a choice must be made as to which two of the variables, inner aspect ratio, outer aspect ratio or core volume fraction will be specified. Inner aspect ratio is always greater than or equal to outer aspect ratio. The ratio of inner aspect ratio over outer aspect ratio becomes larger as the core volume fraction becomes smaller.

Altogether seven variables are used to characterize a confocally coated spheroid. These variables are inner and outer complex refractive indices, core volume fraction, inner aspect ratio and outer aspect ratio. As a result of the confocal constraint only two of the last three variables are independent leaving six independent variables governing extinction. Projecting contours onto a two dimensional plane was an effective technique to locate strong extinction produced by a solid spheroid where there were only three governing independent variables but not when there are six variables. The appropriate procedure for seeking out extinction maxima in six dimensions is to employ a function extrema search algorithm. Such a search is being undertaken and it is too early to describe the results, however it is valuable to portray in two dimensions what happens to the strong extinction observed earlier due to high aspect ratio solid metal spheroids when a dielectric confocal coating is applied over the outside.

Calculations have been made for metal core dielectric coated spheroids and it was found that dielectric coatings reduce extinction at all aspect ratios not close to one for both oblate and prolate spheroids. On the other hand it has been discovered that applying a metal coating over a dielectric core can significantly increase extinction for both prolate and oblate spheroids. Figures 6 and 7 map the extinction difference between coated and uncoated oblate spheroids. Extinction due to solid oblate spheroids with real index 20 and imaginary index 20 is subtracted from the extinction due to coated oblate spheroids with dielectric core real index 1.5 imaginary index 0.01 and metal coating complex refractive index equal to that of the solid spheroid. In figure 6, the solid spheroid aspect ratio is set equal to the inner aspect ratio while in figure 7 it is equal to outer aspect ratio. These contour maps are similar to those of a prolate spheroid except that the contour marking the boundary where extinction of both coated and uncoated become equal occurs at an aspect ratio nearly an order of magnitude smaller. A substantial increase in extinction is evident in figures 6 and 7 as a result of the dielectric core up to aspect ratios of nearly one thousand for core volume fractions between 0.1 and 0.9. At larger aspect ratios the solid spheroid

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is superior, however this cutoff depends on the optical constants of the metal.

In figure 8, we can see what happens to this coated spheroid at an outer aspect ratio of one hundred and core volume fraction of 0.5 when we adjust the core refractive index to determined what improvements are possible over the dielectric core just discussed. The original dielectric core with real index 1.5 and imaginary index 0.01 is in an area of relatively strong extinction but figure 8 shows that by increasing the core imaginary index above 0.01 extinction will get larger. The optimal core would have a small real index and an imaginary index between 5 and 30; values to be expected in a metal a frequencies just below the plasma frequency at visible wavelengths.

As mentioned earlier the Rayleigh ellipsoidal theory is not a good approximation for particles that have edges and vertices such as polyhedra. Fortunately dielectric continuum and lattice dynamical calculations predict the absorption properties of cubes and other polyhedra small compared to wavelength. The results of such calculations for a cube appear in figure 9. Once again resonances emerge along the K axis but now there are six resonances located between imaginary indices of one half and two with the strongest resonance appearing furthest up the axis. Extinction far removed from these resonances or outside the restrahl region is almost indistinguishable from that of a small sphere.

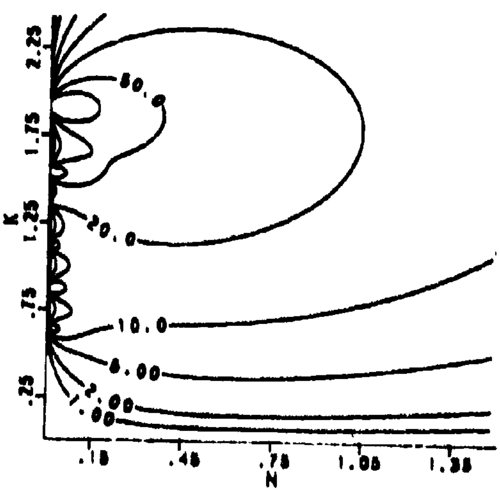

Figure 9. Extinction isopleths fo. a cube as a function of complex refractive index.

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CONCLUSIONS

When particle size becomes small compared to wavelength, extinction not only depends on geometric cross sections but also becomes a very strong function of complex refractive index. Regions of resonant extinction were located in the complex refractive index plane for a variety of spheroidal and confocally coated spheroidal particles using the Rayleigh ellipsoidal approximation. The strongest most extensive is found for high aspect ratio metal prolate and oblate spheroids approximating thin needles and disks. Even stronger extinction was found to occur when metal needles and disks have a dielectric core. On the other hand a dielectric coating reduces extinction. The unbounded peaks of extinction resonances, located where the real part of the complex refractive index becomes zero, were proven to be inaccessible to any material obeying the Kramers-Kroenig relation which requires absorption at restrahl. Finally the six resonances of a cubic particle were explored in the complex refractive index plane. Because a cube is an example of where the Rayleigh ellipsoidal approximation fails most severely, the extinction was predicted using a result taken from the dielectric continuum and the lattice dynamical theories.

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